# (12) UK Patent Application (19) GB (11) 2 113 685 A

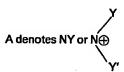
- (21) Application No 8301981
- (22) Date of filing 25 Jan 1983
- (30) Priority data
- (31) 83900 84391
- (32) 26 Jan 1982 27 Sep 1982
- (33) Luxembourg (LU)
- (43) Application published 10 Aug 1983
- (51) INT CL<sup>3</sup> C07C 93/00 103/44// C07D 207/40 303/02
- (52) Domestic classification
  C2C 1300 1341 215 220
  227 22Y 246 250 251 253
  25Y 271 281 290 29X 29Y
  305 30Y 321 322 323 32Y
  332 342 34Y 351 352 360
  361 362 364 36Y 450 453
  45Y 591 592 597 601 602
  610 620 621 623 624 62X
  630 63X 640 650 652 660
  661 662 80Y 819 AA KH
  KR KY LG LW
  U1S 1343 1399 C2C
- (56) Documents cited None
- (58) Field of search C2C
- (71) Applicants
  L'Oreal,
  (France),
  14 rue Royale,
  Paris 75008,
  France.
- (72) Inventors
  Andree Bugaut,
  Alain Genet.
- (74) Agent and/or Address for Service J. A. Kemp and Co., 14 South Square, Gray's Inn, London WC1R 5EU.

(54) 1-substituted phenoxy-3-amino-propan-2-ol derivatives and hair-dyeing compositions containing them

(57) Compounds useful in hair dyeing compositions are represented by the formula:

or an acid addition salt thereof, in which formula

Z represents NO<sub>2</sub> or NH<sub>2</sub>;



X⊕, wherein Y represents two identical or different C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl groups or together with the nitrogen atom of the group NY or



represents a morpholino or piperidono ring or when A represents the group NY, Y may also represent two hydrogen atoms or a halogen atom and a  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl group, Y' represents a  $C_1$ - $C_4$  alkyl group, and X represents an anion; and

 $R_1$  and  $R_2$  are identical or different and represent a hydrogen atom or a  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl radical.

Compounds of the above formula with the proviso that if A denotes NY (1) if Z is in the 4-position on the benzene nucleus and if NR<sub>1</sub>R<sub>2</sub> is in the 2position, R<sub>1</sub> and R<sub>2</sub> both representing a hydrogen atom, (a) one of the two substituents of which Y is composed is not an ethyl group if the other substituent is a hydrogen atom and (b) the group NY does not represent a morpholino or piperidino heterocyclic ring, and (2) if one of the two substituents of which Y is composed denotes a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group and the oth r denot sa C1-C4 alkyl group, Z cannot be located in th 3-positi n and  $NR_1R_2$  in the 2-position,  $R_1$  denoting a hydr gen at m and R2 denoting a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group, are claimed per se.

GB 2 113 685 A

10

25

35

40

45

50

55

60

#### **SPECIFICATION**

New compounds which can be used for hair dyeing, process for the ir preparation, dyeing compositions in which they are present and corresponding hair-dying process

- The present invention relates to new 1-(substituted phenoxy)-3-aminopropan-2-ol compounds in which the extra-nuclear amine group may or may not be substituted, and to the process for their preparation. The invention also relates to hair-dyeing compositions containing these new compounds and to a dyeing process using the said compositions.
- The object of the invention is to propose a new class of compounds which can be used in hair dyes to give strong colourations which are stable to light and have a good fastness to weather and washing. A further object of the invention is to propose a new category of compounds having a good degree of harmlessness and satisfactory characteristics from the point of view of mutagenesis.

The present invention relates to a new chemical compound of the formula (I) (or a corresponding acid salt)

- 25 in which formula:
  - Z represents NO₂ or NH₂;
- A denotes NY or the group
- X<sup>O</sup>, Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent groups having at most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and it also being possible for one or both of the substituents of which Y is composed to represent hydrogen, only if A denotes NY, Y' respresenting a lower alkyl substituent
- 40 group having at most 4 carbon atoms, and X representing an anion; and
   R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a lower alkyl or hydroxyalkyl radical having at most 4 carbon atoms, with the proviso that if A denotes NY, 1°) if Z is in the 4-position on the benzene nucleus and if NR<sub>1</sub>R<sub>2</sub> is in the 2-position, R<sub>1</sub> and R<sub>2</sub> both representing a hydrogen atom, one of the two substituents of which Y is composed does not represent an ethyl group if the other substituent
- represents a hydrogen atom, and the two substituents of which Y is composed do not form a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and 2°) if one of the two substituents of which Y is composed denotes a hydrogen atom or an alkyl group and the other denotes an alkyl group, Z cannot be located in the 3-position and NR<sub>1</sub>R<sub>2</sub> in the 2-position, R1 denoting a hydrogen atom and R<sub>2</sub> denoting a hydrogen atom or an alkyl group.
- X can advantageously be a halogen, in particular chlorine.
  - The present invention also relates to a process for the preparation of a chemical compound of the formula (i) (or a corresponding acid salt) in which:
  - Z represents NO<sub>2</sub> or NH<sub>2</sub>;
- A denotes NY, Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent
   groups having at most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and it also being possible for one or both of the substituents of which Y is composed to represent hydrogen; and
- R<sub>1</sub> and R<sub>2</sub> represent hydrogen atoms, with the proviso that if Z is in the 4-position on the benzine nucleus and if NR<sub>1</sub>R<sub>2</sub> is in the 2-position, one of the twe substituents of which Y is composed does not represent an ethylogroup if the other substituent represents a hydrogen atom, and the two substituents of which Y is composed does not form a morpholine or piperidine ring with the nitrogen atom to which they are attached; the process comprising the following steps:
  - a) epichlor hydrin is r acted with the kn wn compound of the formula (II)

15

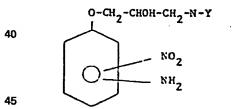
20

10 to give the compound of the formula (III)

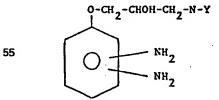
b) an amine of the formula HNY, in which Y has the meaning indicated above, is reacted with the compound of the formula (III) to give the compound of the formula (IV)

25 O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-N-Y NO<sub>2</sub> NHCOCH<sub>3</sub>

 a strong acid, such as hydrochloric acid, is reacted with the compound of the formula (IV) to give the compound of the formula (V)



d) and, if appropriate, to obtain the compound of the formula (I) in which Z represents NH<sub>2</sub>, reduction is carried out either, for example, by means of zinc powder in an alcoholic medium in the presence of ammonium chloride, or by means of catalytic hydrogenation, it being possible for palladium-on-charcoal to be used as the catalyst, and this makes it possible to obtain the compound of the formula (VI)



60 The present invention als relates to a process f rth preparation of a ch mical c mp und fth formula 60 (I) (or corresp nding acid salt) in which:

- Zr pr sents NO2 or NH2;

A denot s NY, Y representing two id ntical or diff r nt lower alkyl or low r hydroxyalkyl substituent
groups having at most 4 carbon atoms, th s tw groups optionally forming a morpholin or piperidine
heterocyclic ring with the nitrogen at mt which they ar attached, and it also being p ssible for one r both 65

10

15

20

25

30

35

40

-10

50

10

15

20

25

30

35

40

45

50

of the substituents of which Y is composed to represent hydr gen; and

-  $R_1$  and  $R_2$  are identical r different and repres nt a hydrogen atom or a 1 w r alkyl or hydroxyalkyl radical having at most 4 carbon atoms, the case in which  $R_1 = R_2 = H$  being excluded, in which process the compound of the f rmula (VII)

10 OH NO<sub>2</sub> R<sub>1</sub> R<sub>2</sub>

in which formula R<sub>1</sub> and R<sub>2</sub> have the meanings indicated above, is used as the starting material, and the reactions involved in steps a) and b) mentioned above are carried out successively to give a product of the formula (VIII)

20 NO<sub>2</sub> R<sub>1</sub> R<sub>2</sub>

in which Y, R<sub>1</sub> and R<sub>2</sub> have the meanings indicated above, and if it is desired to obtain a compound of the formula (I) (or a corresponding acid salt) in which Z represents NH<sub>2</sub>, A denoting NY, the compound of the formula (VIII) is subjected to reduction as indicated in step d) mentioned above. As a variant, if neither of the substituents of which Y is composed represents a hydrogen atom, it is possible to use a process of preparation which starts from a compound of the formula (II), to carry out steps a), b), c) and d) and then to introduce a substituent into one of the nuclear amine groups of the compound of the formula (VI), for example by introducing a substituent into the corresponding arylsulphonamide and subjecting this substituted arylsulphonamide to acid hydrolysis.

35 The present invention also relates to a process for the preparation of a compound of the formula (I) in which:

- Z denotes NO<sub>2</sub> or NH<sub>2</sub>;

40 - A denotes

⊕ ✓ Y

X<sup>O</sup>, Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent groups having at most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, Y' representing a lower alkyl substituent group having at most 4 carbon atoms, and X representing an anion; and

50 - R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a lower alkyl or hydroxyalkyl radical having at most 4 carbon atoms; in which process the nuclear amine group (or groups) of the corresponding tertiary compound is (or are) protected by acetylation, this being followed by reaction with a quaternising agent. Subsequently, the product is deacetylated by reaction with an acid and, if appropriate, the quaternisation anion can be changed at the same time.

In the case where Z represents a nitro group, the compounds of the formula (I) are direct dyestuffs which can be used for dyeing keratin fibres, and in particular hair. It has been found that these compounds have the advantage of good solubility in the solvents generally used in hair dyeing, and this enables them to be used at a sufficiently high concentration to giv the keratin fibre a strong col uratin with a good uniformity. The dying obtained has a good stability to light and weather. Furth rmire, the use of these compounds in hair dyeing is characterised by a good degree of harmlessness. The invention thus also relates to a dyeing composition for keratin fibres, and in particular for hair, which composition contains, in an appropriate carrier, at I ast on compound of the formula (I) (or a correspinding acid salt) in which:

- Z represents a nitro group;
- A denotes NY or



X<sup>O</sup>, Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent groups having at 10 most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and it also being possible for one or both of the substituents of which Y is composed to represent hydrogen, only if A denotes NY, Y' representing a lower alkyl substituent group having at most 4 carbon atoms, and X representing an anion; and

10

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a lower alkyl or hydroxyalkyl radical 15 having at most 4 carbon atoms. In a preferred embodiment, the dyeing composition according to the invention contains from 0.001% to 4% by weight of at least one compound of the formula (I).

15

In the case where Z represents an NH<sub>2</sub> group, the compounds of the formula (I) are either oxidation bases, in the case of para-diamines or ortho-diamines, or couplers intended to be used in association with oxidation bases, in the case of meta-diamines.

20

If the compound of the formula (I) is an oxidation base, the invention also relates to a dyeing composition for keratin fibres, in particular for hair, which composition contains, in an appropriate carrier, at least one compound of the formula (I) (or a corresponding acid salt), in which formula:

- Z represents an NH<sub>2</sub> group;
- A denotes NY or

25



25

30 XO, Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent groups having at most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and it also being possible for one or both of the substituents of which Y is composed to represent hydrogen, only if A denotes NY, Y' representing a lower alkyl substituent group having at most 4 carbon atoms, and X representing an anion; and

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a lower alkyl or hydroxyalkyl radical having at most 4 carbon atoms. In a preferred embodiment, the compound of the formula (I) is used in a proportion of between 0.001% and 4% by weight, relative to the total weight of the composition.

35

In the case where the compound of the formula (I) is a meta-phenylenediamine, the invention also relates to a dyeing composition for keratin fibres, and in particular for hair, containing, in an appropriate carrier, at least one oxidation base, which composition also contains at least one compound of the formula (I) (or a corresponding acid salt), in which formula:

40

- Z represents an NH<sub>2</sub> group;
- A denotes NY or

45



 $X^{\Theta}$ , Y representing two identical or different lower alkyl or lower hydroxyalkyl substituent groups having at 50 most 4 carbon atoms, these two groups optionally forming a morpholine or piperidine heterocyclic ring with the nitrogen atom to which they are attached, and it also being possible for one or both of the substituents of which Y is composed to represent hydrogen, only if A denotes NY, Y' representing a lower alkyl substituent group having at most 4 carbon atoms, and X representing an anion; and

50

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a lower alkyl or hydroxyalkyl radical having at most 4 carbon atoms, with the proviso that if A denotes NY, if Z is in the 4-position on the benzene nucleus and if  $NR_1R_2$  is in the 2-position,  $R_1$  and  $R_2$  both representing a hydrogen atom, one of the two substituents of which Y is composed does not represent an ethyl group if the other substituent represents a hydrogen atom, and the two substituents of which Y is composed do not form a morpheline or piperidine heterocyclic ring with the nitrogen atom to which they are attached. The compound of the formula (I) is 60 preferably used in a proportion of betw en 0.001% and 2.5% by weight, relative to the total weight of the comp sition.

55

The dyeing compositions according to the invention can comprise, in addition to the compounds of the f rmula (I), oxidati n bases consisting of:

A - Para-phenylenediamines f the general formula (IX)

5

or the corresponding acid salts, in which formula R'<sub>1</sub>, R'<sub>2</sub> and R<sub>3</sub> are identical or different and represent a hydrogen atom, an alkyl radical having from 1 to 4 carbon atoms, an alkoxy radical having 1 or 2 carbon atoms or a halogen atom, and R<sub>4</sub> and R<sub>5</sub> are identical or different and represent a hydrogen atom, an alkyl or hydroxyalkyl radical, an alkoxyalkyl radical in which the alkoxy group contains 1 or 2 carbon atoms, or a carbamylalkyl, alkylsulphonamidoalkyl, acetylaminoalkyl, ureidoalkyl, carbethoxyaminoalkyl, aminoalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl or morpholinoalkyl radical, the alkyl groups in R<sub>4</sub> and R<sub>5</sub> having from 1 to 4 carbon atoms, or alternatively R<sub>4</sub> and R<sub>5</sub> form a piperidino or morpholino group together with the nitrogen atom to which they are attached, with the proviso that R'<sub>1</sub> and R<sub>3</sub> respresent a hydrogen atom if R<sub>4</sub> and R<sub>5</sub> do not represent a hydrogen atom.

20

15

B - Para-aminophenols of the general formula (X)

25

30

25

or the corresponding acid salts, in which formula R<sub>6</sub> represents a hydrogen atom, an alkyl radical containing from 1 to 4 carbon atoms or a halogen atom such as, for example, chlorine or bromine.

35

30

C - Heterocyclic bases such as 2,5-diaminopyridine, 3-methyl-7-aminobenzomorpholine and 5-aminoindole.

In addition to the compounds of the formula (I), the dyeing compositions according to the invention can contain the following products, taken in isolation or in combination: 40

if the composition contains at least one oxidation base: at least one coupler taken from the group comprising resorcinol, pyrocatechol, 2-methylresorcinol, 2-ethylresorcinol, meta-aminophenol, 2-methyl-5-aminophenol, 2-methyl-5-N-(β-hydroxyethyl)-aminophenol, 6-hydroxybenzomorpholine, 2,6-dimethyl-3-acetylaminophenol, 2-methyl-5-carbethoxyaminophenol, 2-methyl-5-ureidophenol, 2-diaminophenoxyethanol, 2,4-diaminoanisole, 2,6-dimethyl-meta-phenylenediamine, 2-amino-4-N-methylaminophenoxyethanol, 2,4-diaminophenyl β-methoxyethyl ether, 2,4-diaminophenyl β-mesylaminoethyl ether, 2-N-carbamylmethylamino-4-aminoanisole, 3-amino-4-methoxyphenol, α-

45

50 2-amino-4-N-(β-hydoxyethyl)-aminophenyl β-hydroxypropyl ether;
2) ortho-phenylenediamines and ortho-aminophenols optionally containing substituents on the nucleus or on the amine groups, or ortho-diphenol, it being possible, by means of complex oxidation mechanisms, for these products to lead to new coloured compounds, either by cyclisation with themselves or by reaction with para-phenylenediamines;

naphthol, 2,6-diaminopyridine, 3,5-diamino-2,6-dimethoxypyridine, 1-phenyl-3-methylpyrazol-5-one and

50

3) dyestuff precursors of the benzene series, containing, on the nucleus, at least three substituents chosen from the group comprising hydroxyl, methoxy or amino groups, such as 2,6-diaminohydroquinone dihydochloride, 2,6-diamino-4-N,N-bis-(ethyl)-aminophenol trihydrochloride, 2,4-diaminophenol dihydrochloride, 2,6-diamino-4-N,N-bis-(ethyl)-aminophenol trihydrochloride, 2,6-diaminophenol dihydrochloride, 2,6-diaminophenol dihydrochl

55

loride, 1,2,4-trihydroxybenzene, 2,3,5-trihydroxytoluene or 4-methoxy-2-amino-N-(β-hydroxyethyl)-aniline;
4) quinone dy stuffs such as 2-hydroxy-1,4-naphthoquinone, 5-hydroxy-1,4-naphthoquinone and 2-[4'-60 (N,N-dihydr xyethylamino)-anilino]-5-N'-(β-hydroxyethyl)-amino-1,4-benz quin ne;

60

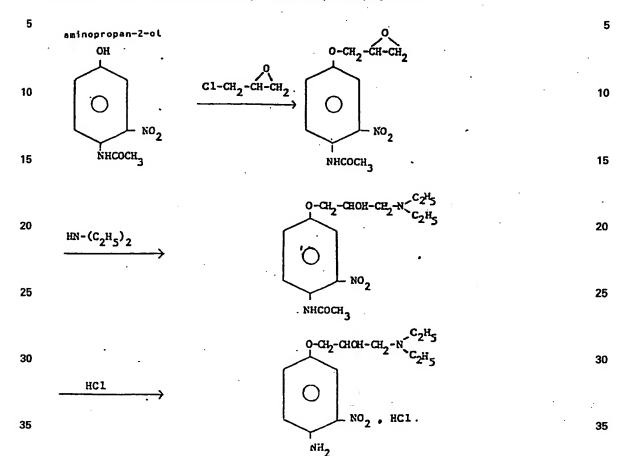
5) indoanilines, indophenols or indamines, or their leuc derivatives, such as 4,4'-dihydroxy-2-amin -5-methyldiphenylamine, 4,4'-dihydroxy-2-N-(β-hydr xyethyl)-amino-5-methyl-2'-chlorodiph nylamine, 2,4'-diamino-4-hydroxy-5-methyldiphenylamine, 2,4-dihydroxy-4'-N-(β-methoxyethyl)-aminodiphenylamine and 2,4-dihydroxy-5-methyl-4'-N-(β-methoxyethyl)-amin diphenylamine;

6) direct dy stuffs chosen fr in the class of the azo dyestuffs, the anthraquin ine dyestuffs and the nitro

	dyestuffs of the benzene series, such as 2-amino-3-nitrophenol, 1-amino-2-nitro-4-N- $(\beta$ -hydroxyethyl)-amino-5-methylbenzene, 1-N,N-bis- $(\beta$ -hydroxyethyl)-amino-3-nitro-4-N'-methylaminobenzen , 1-N-methyl-N- $(\beta$ -hydroxyethyl)-amino-3-nitro-4-N'- $(\beta$ -hydroxyethyl)-amino-3-nitro-4-N'-methylaminobenzene, 3-nitro-4-N- $(\beta$ -hydroxyethyl)-aminoanisole, 3-nitro-4-N- $(\beta$ -hydroxyethyl)-a	٠
5		5
	7) various customary adjuvants such as water, penetrating agents, surface-active agents, thickeners, antioxidants, alkalising or acidifying agents, perfumes, sequestering agents, film-forming products and	
10	treating agents.  The pH of the dyeing compositions according to the invention is between 5 and 11.5. Amongst the alkalising agents which can be used, there may be mentioned ammonia, alkylamines such as ethylamine or triethylamine, alkanolamines such as mono-, di- or tri-ethanolamine, alkylalkanolamines such as methyldiethanolamine, the hydroxides of sodium or potassium and the carbonates of sodium, potassium or	10
15	ammonium. Amongst the acidifying agents which can be used, there may be mentioned lactic acid, acetic acid, tartaric acid and phosphoric acid.	15
20		20
	monium bromide and cetylpyridinium bromide, fatty acid diethanolamides or polyoxyethyleneated or polyglycerolated acids, alcohols or alkylphenols. Preferably, the surface-active agents are present in the composition according to the invention in a proportion of between 0.5 and 55% by weight and advantageously of between 4 and 40% by weight, relative to the total weight of the composition.	20
25	One-of- and tracks are also be added at the control of the state of th	25
30	total weight of the composition.  The thickening products which can be added to the composition according to the invention can advantageously be taken from the group comprising sodium alginate, gum arabic, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose and the sodium salt of carboxy-	30
35	weight of the composition, and advantageously of between 0.5 and 3% by weight.  The antioxidants which can be added to the composition according to the invention can advantageously	35
40	be taken from the group comprising sodium sulphite, thioglycolic acid, mercaptosuccinic acid, sodium bisulphite, ascorbic acid and hydroquinone. These antioxidants can be present in the composition in a proportion of between 0.05 and 1.5% by weight, relative to the total weight of the composition. If the dyeing composition according to the invention contains at least one oxidation base, it contains, at the time of use, oxidising agents such as hydrogen peroxide, urea peroxide or per-salts such as ammonium persulphate.	40
45	The dyeing composition according to the invention can be present in the form of a liquid, a cream, a gel or an aerosol or in any other form suitable for dyeing keratin fibres.  The present invention also relates to a new hair-dyeing process, characterised in that the dyeing composition defined above is left to act on the hair for an application time varying between 10 and 45	45
50	minutes, and in that the hair is rinsed, optionally washed and rinsed again, and dried.  In the case where the dyeing composition used contains at least one oxidation base, the abovementioned process includes an initial stage in which a sufficient amount of oxidising agents is mixed with the said composition at the time of use.	50
	To provide a clearer understanding of the object of the invention, several embodiments thereof will now be described by way of purely illustrative and non-limiting examples.	

# **EXAMPLE 1**

# Preparation of 1-(3'-nitro-4'-aminophenoxy)-3-N,N-diethylaminopropan-2-ol



40

# FIRST STEP

Preparation of 1-(3'-nitro-4'-acetylarninophenoxy)-2,3-epoxypropane

150 ml of epichlorohydrin are added, at ambient temperature, to a solution of 0.376 mol (73.7 g) of 3-nitro-4-acetylaminophenol in 375 ml of 1.1 N sodium hydroxide solution. The reaction medium is left to stand at ambient temperature for 48 hours, with thorough stirring, and the expected product which has precipitated is then filtered off. After drying in vacuo and recrystallisation from benzene, this product melts at 123°C.

The product obtained corresponds to the following analysis results:

50		Calculated for		. 50
	Analysis	$C_{11}H_{12}N_2O_5$	Found	00
	C%	52.38	52.32	
	Н%	4.80	4.77	
55	N%	11.11	11.06	55
	Ο%	31.72	31.57	•

#### **SECOND STEP**

Preparation of 1-{3'-nitro-4'-acetylaminophenoxy}-3-N,N-diethylaminopropan-2-ol

60 0.2 mol (50.4 g) f 1-(3'-nitro-4'-acetylaminophen xy)-2,3-ep xypr pane is heated for 3 hours und r reflux in 146 g f diethylamine and 50 ml of absolute alcohol. The diethylamine and the alcohol are driven off in vacuo. Th residual oil crystallises sl wly. After recrystallisati n from cyclohexane, 58 g of the expected product, which melts at 77°C, ar btained.

The product obtained corresponds to the following analysis results:

	Analysis	Calculated for C <sub>15</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub>	Found	
5	C%	55.37	55.40	5
	H%	7.13	7.18	
	N%	12.92	12.86	
	О%	24.59	24.78	

10 THIRD STEP

10

15

30

60

65

Preparation of 1-(3'-nitro-4'-aminophenoxy)-3-N,N-diethylaminopropan-2-ol hydrochloride 0.152 mol (49.7 g) of 1-(3'-nitro-4'-acetylaminophenoxy)-3-N,N-diethylaminopropan-2-ol is heated for 30 minutes, in a boiling water-bath, in 100 ml of hydrochloric acid (specific gravity = 1.18). After the addition of 15 ammonia to the reaction medium so as to give a pH of 6, the 1-(3'-nitro-4'-aminophenoxy)-3-N,Ndiethylaminopropan-2-ol monohydrochloride crystallises. It is filtered off, washed with a small amount of 80°

strength alcohol, recrystallised from a mixture of water and ethanol and dried in vacuo. It melts at 178°C.

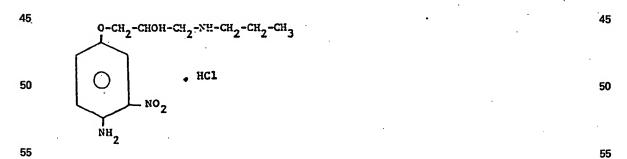
The product obtained corresponds to the following analysis results:

20	•	Calculated for		20
	Analysis	$C_{13}H_{21}N_3O_{4}HCI$	Found	
	C%	48.82	48.65	
	H%	6.93	6.90	
25	N%	13.14	12.90	25
	O%	20.01	20.17	2.5
	CI%	11.09	10.96	

#### **EXAMPLE 2**

30 Preparation of 1-(3'-nitro-4'-aminophenoxy)-3-N-propylaminopropan-2-ol monohydrochloride

O-CH2-CHCH-CH2-NH-CE 35 35 HC1 NO2 40 NO2 40 инсосн3 инсосн3



#### FIRST STEP

60 Preparation of 1-(3'-nitro-4'-acetylaminophenoxy)-3-N-propylaminopropan-2-ol 0.02 mol (5.0 g) of 1-(3'-nitro-4'-acetylamin phenoxy)-2,3-epoxypr pane, btained according to the first step f Example 1, is introduced into 25 ml of N-pr pylamine and th mixture is then heat df r 3 hours at 45°C. The reaction medium is subsequently poured into 100 g of iced water, and the expected product which has precipitat disthen filt red off and washed with water. After drying in vacuo and recrystallisation from a 65 mixtur f benzene and ethyl acetat, the product milts at 146°C.

65

# The product obtained corresponds to the fill wing analysis results:

	Analysis	Calculated for C <sub>14</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub>	Found	
5	C%	54.01	54.00	5
	. H%	. 6.80	6.86	
	. 11% N%	13.50	13.36	•
	0%	25.70	25.88	
	0%	23.70	25.00	8-
10	SECOND STEP	•		10
		ninophenoxy)-3-N-propylaminopropa	n 2 al manahydraehlarida	
		o-4′-acetylaminophenoxy)-3-N-propy		
		th, in 7 ml of hydrochloric acid (specific		
			o a pH of 5. The monohydrochloride of	
15			all amount of 80° strength alcohol and	15
		ture of water and ethanol. It melts at 22		
	The product obtained corre	sponds to the following analysis result	S:	
		Coloulated for		
<b>20</b> .	Amakada	Calculated for	Farmed	20
	Analysis	C <sub>12</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> HCl	Found	
		477.4.4	47.04	
	· C%	47.14	47.24	
	Н%	6.59	6.57	
25	N%	13.74	13.75	25
	0%	20.93	20.76	
	CI%	11.60	11.55	•
	EXAMPLE 3		•	
30	Preparation of 1-(3'-nitro-4'-ai	minophenoxy)-3-aminopropan-2-ol		30
			·	
•	0	•		
	, / ·	C-CH <sub>2</sub>		
	O-CH <sub>2</sub> -CH-CH <sub>2</sub>	/ 12	•	
35		HN	•	35
		Ç-CH <sub>2</sub>	•	
		Ö ²		
40	NO <sub>2</sub>			40
40	2			40
	1			
	инсосн 3			
45		0	•	45
45		O .C-CH <sub>o</sub>	·	40
	о-сн <sub>2</sub> -снон-сн	<i></i>		
	1		arou_Ci	
		6 2 0-CH	2-CHOH-CH <sub>2</sub>	
50	[ ]		NH 2	50
30			2	-
		HC1		
	NO <sub>2</sub>	. — /		
	~ '	L ,	⊥ NO <sub>2</sub>	
55	NHCOCH <sub>3</sub>	$\checkmark$	-	55
	3	ин <sub>2</sub>	•	
			•	

Preparation of 1-(3'-nitro-4'-acetylaminophenoxy)-3-succinimido-3-propan-2-ol
50.4 q (0,2 m l) f1-(3'-nitro-4'-acetylaminophenoxy)-2.3-ep xypropane (prepared a

50.4 g (0.2 m l) f1-(3'-nitro-4'-acetylaminophenoxy)-2,3-ep xypropane (prepared according to the first step f Example 1) are introduced int 150 ml of absolute ethanol to which 12 drops f pyridine have been added. 0.24 mole (23.7 g) of succinimide is added. The mixture is heated under reflux for 5 hours 30 minutes. On cooling, the expect d product crystallises. It is filter d off and washed with a small amount of alc h l.

20

30

After recrystallisation from alcohol and drying in vacuo, it melts at 154°C.

The product obtained corresp nds to the following analysis results:

5	Analysis	Calculated for C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub>	Found	5
	C%	51.28	51.34	
	H%	4.88	4.95	
	N%	11.96	11.86	
10	O%	31.83	31.84	10
				10

#### **SECOND STEP**

Preparation of 1-(3'-nitro-4'-aminophenoxy)-3-aminopropan-2-ol

50.9 g (0.145 mol) of the succinimido derivative obtained according to the first step are introduced into 100 ml of 96° strength alcohol to which 250 ml of hydrochloric acid (specific gravity = 1.18) have been added. After 14 hours under reflux, the cooled reaction medium is treated with acetone. The expected product precipitates in the form of the hydrochloride. This hydrochloride is taken up in 70 ml of water. By rendering the aqueous solution alkaline with 10 N sodium hydroxide solution, the 1-(3'-nitro-4'-aminophenoxy)-3-aminopropan-2-ol is precipitated in the form of an oil, which crystallises rapidly. After recrystallisation from alcohol, the product melts at 124°C.

The product obtained corresponds to the following analysis results:

	Analysis	Calculated for C <sub>3</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub>	Found	
25	C% H% N% O%	47.57 5.77 18.49 28.17	47.57 5.73 18.36 28.18	. 25

30 EXAMPLE 4 Preparation of 1-(2'-amino-4'-nitrophenoxy)-3-aminopropan-2-ol

15

35

50

55

#### FIRST STEP

Preparation of 1-(2'-acetylamino-4'-nitrophenoxy)-2,3-epoxypropane

1.6 litres of epichl r hydrin ar added t a soluti n of 2 mols (392 g) f 2-acetylamino-4-nitr phen I in tw litres of 1.1 N sodium hydroxide solution, and the reaction medium is left to stand for 96 hours at 20°C, with 5 thorough stirring. 282 g of the expected product which has precipitated are filtered off and washed with water. This product contains about 20% of a by-product, namely 1,3-bis-(2'-acetylamino-4'-nitrophenoxy)-propan-2-ol (melting at 233°C), which results from the condensation of one molecule of epichlorohydrin with two mols of 2-acetylamino-4-nitrophenol. However, it will be used as such for the second step of the synthesis, the by-product being very readily removed at this stage.

10 SECOND STEP

Preparation of 1-(2'-acetylamino-4'-nitrophenoxy)-3-succinimidopropan-2-ol

100 g of the crude product obtained in the previous step are introduced into 500 ml of 95° strength ethanol. 0.52 mol (51.5 g) of succinimide and 2.5 ml of pyridine are added and the mixture is heated under reflux for 2 hours, with stirring. The alcoholic solution is filtered at the boil to isolate the expected product, which is insoluble in hot alcohol. This gives 60 g of virtually pure 1-(2'-acetylamino-4'-nitrophenoxy)-3-succinimidopropan-2-ol. After recrystallisation from alcohol, this product melts at 184°C.

The product obtained corresponds to the following analysis results:

20	·	Calculated for		20
20	Analysis	$C_{15}H_{17}N_3O_7$	Found	20
	C%	51.28	51.15	
	Н%	4.84	4.87	
25	N%	11.96	11.86	25
	0%	31.91	32.15	

The mother liquors from the reaction medium contain a small amount of succinimido derivative together with 1,3-bis-(2'-acetylamino-4'-nitrophenoxy)-propan-2-ol, which has thus been removed.

30 THIRD STEP

Preparation of 1-(2'-amino-4'-nitrophenoxy)-3-succinimido-propan-2-ol

2 g (0.0057 mol) of the 1-(2'-acetylamino-4'-nitrophenoxy)-3-succinimidopropan-2-ol obtained in the second step are heated for one hour, in a boiling water-bath, in 10 ml of hydrochloric acid (specific gravity = 1.18), with stirring. After the reaction medium has been cooled, diluted and rendered alkaline, the expected product precipitates. It is filtered off, washed with water and recrystallised from ethanol. It melts at 200°C. The product obtained corresponds to the following analysis results:

40	Analysis	Calculated for C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O <sub>8</sub>	Found	40
	C%	50.48	50.47	
	Н%	4.85	4.87	
	N%	13.59	13.58	
45	О%	31.07	30.94	45

#### **FOURTH STEP**

Preparation of 1-(2'-amino-4'-nitrophenoxy)-3-aminopropan-2-ol

7.9 g (0.0256 mol) of the succinimido derivative prepared in the previous step are heated for 8 hours in 40 ml of hydrochloric acid (specific gravity = 1.18) under reflux, with stirring. After the reaction medium has cooled, the expected product, which has crystallised in the form of the dihydrochloride, is filtered off. This dihydrochloride is dissolved in 175 ml of water and the pH is brought to 9 with sodium hydroxide solution. The expected product which has precipitated is filtered off. After washing with water and recrystallisation from alcohol, the product melts at 159°C.

55 The product obtained corresponds to the following analysis results:

	Analaysis	Calculated for C <sub>9</sub> H <sub>13</sub> N <sub>3</sub> O₄	Found	
60	C%	47.58	47.57	60
-	H%	5.73	5.75	
	N%	18.50	18.56	
	0%	28.19	28.16	

50

55

#### **EXAMPLE 5**

12

Preparation of 1-(2'-amino-5'-nitrophenoxy)-3-aminopropan-2-of

#### FIRST STEP

35 Preparation of 1-(2'-acetylamino-5'-nitrophenoxy)-2,3-epoxypropane
0.376 mol (73.7 g) of 2-acetylamino-5-nitrophenol is dissolved in 375 ml of 1.1 N sodium hydroxide
solution, and 300 ml of epichlorohydrin are then added. The reaction medium is left to stand for 96 hours at
20°C, with thorough stirring, and the exposed product which has precipitated is then filtered off and washed
with water. After recrystallisation from ethanol and drying in vacuo, it melts at 164°C.

40 The product obtained corresponds to the following analysis results:

	Analysis	Calculated for C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	Found	• .
45	C%	52.38	53.29	45
	H%	4.80	4.83	45
	N%	11.11	11.20	
	O%	31.72	31.86	

# 50 SECOND STEP

Preparation of 1-(2'-acetylamino-5'-nitrophenoxy)-3-succinimidopropan-2-ol

0.072 mol (18.2 g) of 1-(2'-acetylamino-5'-nitrophenoxy)-2,3-epoxypropane is introduced into 60 ml of absolute ethanol to which 6 drops of pyridine have been added. 0.087 mol (8.6 g) of succinimide is added and the mixture is then heated under reflux for 5 hours. After cooling, 150 ml of water are added and the alchol is driven off in vacuo. The expected product, which is obtained initially in the form of a water-insoluble oil, crystallises slowly. It is filtered off and recrystallised from 96° strength alcohol. After drying, it melts at 157°C.

The product obtained corresponds to the following analysis results:

60	Analysis	Calculated for C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub>	Found	60
	C%	51.28	51.30	
	H%	4.88	4.94	•
	N%	11.96	11.89	
65	0%	31.88	32.07	65

10

20

60

#### THIRD STEP

Preparation of 1-(2'-amino-5'-nitrophenoxy)-3-aminopropan-2-ol

7.0 g (0.02 m I) of the succinimido derivative obtained in the second step are heated under reflux f r 14 hours in 14 ml of 96° str ngth alcohol to which 38 m of hydrochloric acid (specific gravity = 1.18) have been added. The reaction medium is then cooled and treated with acetone in order to precipitate the expected product in the form of the hydrochloride. This hydrochloride is filtered off and then dissolved in 12 ml of water. By rendering the aqueous solution alkaline with 10 N sodium hydroxide solution, the 1-(2'-amino-5'-nitrophenoxy)-3-aminopropan-2-ol is precipitated in the form of an oil, which crystallises rapidly. The product is filtered off, washed with water and recrystallised from ethanol. It melts at 141°C.

10 The product obtained corresponds to the following analysis results:

	Analysis	Calculated for C <sub>3</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub>	Found .	
15	C%	47.57	47.58	15
13	Н%	5.77	5.76	15
	N%	18.49	18.62	
	0%	28.17	28.28	

20 EXAMPLE 6
Preparation of 1-(2'-amino-5'-nítrophenoxy)-3-N-(β-hydroxyethyl)-aminopropan-2-ol

45
$$\begin{array}{c}
 & \text{NH}_2 \\
 & \text{O-CH}_2\text{-CHOH-CH}_2\text{-NH-CH}_2\text{-CH}_2\text{-OH}
\end{array}$$
50
$$\begin{array}{c}
 & \text{HC1} \\
 & \text{NH}_2\text{OH}
\end{array}$$
50

55 FRST STEP 55

Preparation of 1-(2'-acetylamino-5'-nitrophenoxy)-3-N-(β-hydroxyethyl)-aminopropan-2-ol
10.1 g (0.04 mol) of th 1-(2'-acetylamino-5'-nitrophenoxy)-2,3-ep xypropane pr pared according t th
first stag f Example 5 are dissolved in 36.6 g f monoethan lamine and 10 ml of absolute alcoh I by
heating in a boiling water-bath. After heating for 1 hour 30 minutes in the boiling water-bath, the r action
m dium is poured into 300 g fixed water. The xpect d partially deacetylated pr duct precipitates. It is
filtered off, washed with water and dried in vacuo. It will be used as such for the second stag f the
synthesis.

35

55

#### **SECOND STEP**

Preparation of 1-(2'-amino-5'-nitrophenoxy)-3-N-(β-hydroxyethyl)-aminopropan-2-ol

8.7 g of the crude product obtained in the first stage of the synthesis are heated for 30 minutes, in a billing water-bath, in 22 ml of hydrochloric acid (specific gravity = 1.18). The cooled reaction mixture is treated with 5 ammonia up to a pH of 6. The expected product precipitates in the form of the monohydrochloride. This monohydrochloride is filtered off, recrystallised from an ethanol/water mixture and dried in vacuo. It melts at 156°C.

The monohydrochloride is dissolved in 20 ml of water. The aqueous solution is rendered alkaline with 20% strength ammonia solution. The 1-(2'-amino-5'-nitrophenoxy)-3-N-(β-hydroxyethyl)-aminopropan-2-ol pre-10 cipitates. The product is filtered off, washed with water, recrystallised from water and dried in vacuo. It melts 10 at 177°C.

The product obtained corresponds to the following analysis results:

15	Analysis	Calculated for C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	Found	15
	C%	48.70	48.65	
	H%	6.32	6.25	
	N%	15.49	15.44	
20	0%	29.49	29.33	. 20

#### **EXAMPLE 7**

Preparation of 1-(2',5'-diaminophenoxy)-3-aminopropan-2-ol trihydrochloride

35 7.5 g of zinc powder and a solution of 0.3 g of ammonium chloride in 1.5 ml of water are added to 15 ml to 96° strength alcohol. The mixture is heated to the reflux temperature, with stirring, and 0.015 mol (3.4 g) of the 1-(2'-amino-5'-nitrophenoxy)-3-aminopropan-2-ol prepared according to Example 5 is then added gradually so as to maintain the reflux without external heating. When the addition has ended, the reflux is 40 maintained for 5 minutes and the boiling reaction medium is then filtered into 4.6 ml of iced hydrochloric 40 acid (specific gravity = 1.18). The expected product crystallises in the form of the trihydrochloride. The product is filtered off, washed with alcohol and dried in vacuo. It melts with decomposition at 216-218°C. The product obtained corresponds to the following analysis results:

45	•	Calculated for		45
-	Analysis	C <sub>9</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> ·HCI	Found	.0
	C%	35 <b>.2</b> 5	34.97	
	H%	5.92	5.86	
50	N%	13.70	13.82	50
	0%	10.43	<b>10.68</b> .	30
	CI%	34.69	34.52	

#### **EXAMPLE 8**

55 Preparation of 1-(2',4'-diaminophenoxy)-3-aminopropan-2-ol trihydrochloride

20

60

65

0.02 mol (5.3 g) of the 1-(2'-amino-4'-nitrophenoxy)-3-aminopropan-2-oi monohydrochloride prepared according to Example 4 is introduced into 50 ml of 96° strength alcohol and 0.2 g of 10% strength palladium-on-charcoal. The mixture is heated at 85°C for one hour under 35 bars of hydrogen. After cooling, it is filt red to rem v the catalyst, th filtrate being collected in 20 ml of iced ethanol saturated with 5 hydrogen chloride. The expected product precipitates in the form of the trihydrochloride. After recrystallisation of this trihydrochloride from an ethanol/water mixture, it melts with decomposition at 236-238°C. The product obtained corresponds to the following analysis results:

10	Analysis	Calculated for C <sub>B</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> .3HCl	Found	10
	C%	35.23	35.41	
	Н%	5.87	5.90	
	N%	13.70	13.63	
15	O%	10.44	10.63	15
••	CI%	34.75	34.85	15

It has been found, surprisingly, that this compound, which constitutes a coupler, gives, on coupling with para-aminophenol, much redder tints than its homologue which does not contain an OH group on the side 20 chain; it has also been found, surprisingly, that the red tints obtained are much more stable than in the case of the non-hydroxylated homologue.

#### **EXAMPLE 9**

Preparation of 1-(3'-methylamino-4'-nitrophenoxy)-3-amino-propan-2-ol hydrochloride

# 60 FIRST STEP

Preparation of 1-(3'-methylamino-4'-nitrophenoxy)-2,3-epoxypropane

0.15 mol (36.3 g) f 3-N-m thylamino-4-nitr phenyl β,γ-dihydroxypropyl th r (product described in Example 2 f French Pat int Application 80/17,617) is dissolved in 150 ml f pyridin at ambient temperature. 0.22 m (25.2 g) of methan sulph nyl chl ride is add d dropwise, in the c urse of 10 minutes and with 65 stirring, t this pyridine solution kept at -5°C. When the addition has indicate distribution that the description of the reaction

35

40

medium is allowed to rise t about 20°C, and th n, after th reaction medium has been left to stand for 45 minutes at ambient t mperature, 100 ml of 27.8% strength methanolic solution of sodium methylate are added th reto, at -5°C, in the course of 10 minutes. When the addition has ended, the mixture is stirred for 2 h urs at ambient temperature and the methylene chloride is then washed with water, with 1 N hydrochloric acid solution and then with a saturated solution of sodium bicarbonate. The methylene chloride is driven off in vacuo. The expected product, consisting of the residual oil, crystallises very rapidly. After recrystallisation from ethyl acetate and drying in vacuo, it melts at 113°C.

The products obtained corresponds to the following analysis results:

10	Analysis	Calculated for C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	Found	10
15	C% H% N% O%	53.57 5.39 12.50 28.54	53.66 5.35 12.48 28.58	15

#### SECOND STEP

Preparation of 1-(3'-methylamino-4'-nitrophenoxy)-3-succinimidopropan-2-ol

20 0.087 mol (19.5 g) of 1-(3'-methylamino-4'-nitrophenoxy)-2,3-epoxypropane is dissolved in 75 ml of absolute alcohol to which 6 drops of pyridine have been added. 0.10 mol (10.1 g) of succinimide is added and the mixture is then heated under reflux for 4 hours. The reaction mixture is filtered at the boil. On cooling of the filtrate, the expected product crystallises. After recrystallisation from alcohol and drying in vacuo, it melts at 152°C.

25 The product obtained corresponds to the following analysis results:

	Analysis	Calculated for C <sub>1¢</sub> H <sub>17</sub> N <sub>3</sub> O <sub>8</sub>	Found	
30	C%	52.01	51.97	30
	H%	5.30	5.36	30
	N%	13.00	12.98	
	0%	29.69	29.50	

#### 35 THIRD STEP

Preparation of 1-(3'-methylamino-4'-nitrophenoxy)-3-amino-propan-2-ol monohydrochloride

10.5 g (0.0324 mol) of the succinimido derivative obtained according to the second step are heated under reflux for 7 hours in 20 ml of 96° strength alcohol and 60 ml of 36% strength hydrochloric acid. The reaction medium is cooled to 0°C. The expected product crystallises. It is filtered off, washed with acetone and recrystallised from a mixture of water and alcohol. After drying in vacuo, it melts with decomposition at between 258 and 260°C.

The product obtained corresponds to the following analysis results:

45	Analysis	Calculated for C <sub>10</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> HCl	Found	45
	C%	43.25	43.21	
	Н%	5.81	5.78	
	N%	15.13	15.11	
50	0%	23.04	23.10	50
	CI%	12.77	12.70	50

#### **EXAMPLE 10**

Preparation of 1-(2',4'-diaminophenoxy)-3-dimethylamino-propan-2-ol trihydrochloride monohydrate

#### FIRST STEP

Preparation of 1-)2'-amino-4'-nitrophenoxy)-3-dimethylaminopropan-2-ol

0.085 mol (21.5 g) of 1-(2'-acetylamino-4'-nitrophenoxy)-2,3-epoxypropane (compound described in Example 4) is introduced into 100 ml of a 40% strength aqueous solution of dimethylamine, and the reaction mixture is stirred for 30 minutes at ambient temperature. After dilution by the addition of 225 ml of iced water, followed by neutralisation with acetic acid, the mixture is evaporated to dryness in vacuo. The dried residue is taken up in 150 ml of ethyl acetate. After washing with acetone, the material which is insoluble in ethyl acetate consists of 28.5 g of 1-(2'-acetylamino-4'-nitrophenoxy)-3-dimethylaminopropan-2-ol. This acetylated derivative is heated under reflux for two hours in 220 ml of ethanol saturated with hydrogen chloride. After the reaction medium has cooled, the expected product in the form of the hydrochloride is filtered off. After this hydrochloride has been dissolved in water and the aqueous solution has been rendered alkaline with sodium hydroxide solution, the 1-(2'-amino-4'-nitrophenoxy)-3-dimethylaminopropan-2-ol is

The product is filtered off, washed with water and dried in vacuo. It melts at 123°C. Elementary analysis gives the following results:

45	Analysis	Calculated for C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>	Found	45
	C% -	51.76	51.65	
	H%	6.67	6.72	
	N%	16.47	16.40	
50	O%	25.10	25.02	50

#### SECOND STEP

Preparation of 1-(2',4'-diaminophenoxy)-3-dimethylamino-propan-2-ol trihydrochloride monohydrate
A solution of 0.12 mol (30.6 g) of 1-(2'-amino-4'-nitrophenoxy)-3-dimethylaminopropan-2-ol in 92 ml of
absolute alcohol is subjected to catalytic hydrogenation at 80°C, under a pressure of 40 bars of hydrogen, in
the presence of 4.5 g of 10% strength palladium-on-charcoal. The catalyst is removed by filtration, the
alcoholic filtrate being received in 143 ml of iced ethanol saturated with hydrogen chloride. The expected
product precipitates in the f rm fth trihydrochl ride. This trihydrochloride is filter d off and recrystallised
from an aqueous-alcoh lic soluti n f hydr chl ric acid. After drying in vacuo, it melts with decomposition
at between 205 and 206°C.

#### Elem ntary analysis gives the f llowing results:

	Analysis	Calculated for C <sub>11</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> .3HCl.H <sub>2</sub> O	. Found	
5	C%	37.44	37.31	. 5
	H%	6.81	6.87 ·	
	N%	11.91	11.79	
	0%	13.62	13.89	
10	CI%	30.21	30.07	10

#### **EXAMPLE 11**

Preparation of 2-hydroxy-3-(2',4'-diaminophenoxy)-propyltrimethylammonium chloride dihydrochloride hemihydrate

15

$$\begin{array}{c}
 & CH_3 \\
 & O-CH_2-CHOH-CH_2-N \\
 & CH_3 \\$$

# FIRST STEP

Preparation of 1-(2',4'-diacetylaminophenoxy)-3-dimethylaminopropan-2-ol

Under the conditions described in the second step of Example 10, an alcoholic solution of 0.1 mol (25.5 g) of 1-(2'-amino-4'-nitrophenoxy)-3-dimethylaminopropan-2-ol is subjected to catalyst hydrogenation in the presence of palladium-on-charcoal. The catalyst is removed by filtration, the solvent is driven off in vacuo, th oily residue is tak n up in 200 ml of ethyl acetat , and 17 ml of acetic anhydride ar added gradually thereto. The expect d diacetylat d derivative pr cipitat s in the form of crystals. It is filtered ff, washed with acetone and dried in vacuo. It melts at 118-120°C.

5

	SECOND STEP
	Preparation of 2-hydroxy-3-(2',4'-diacetylaminophenoxy)-propyltrimethylammonium iodide monohydrate
	0.03 mol (9.3 g) of the diacetylated d rivativ obtained in the first step is dissolved in 30 ml of acetone to
	which 3 ml f water has been added. The s lution is heated to 50°C and 0.06 mol (3.75 ml) f methyl iodide is
;	then added thereto, with stirring. The reaction medium is kept at 50°C for 30 minutes. The expected
	quaternary derivative precipitates. It is filtered off, washed with acetone and dried. It melts with
	decomposition at between 159 and 160°C.

Elementary analysis gives the following results:

10	Analysis	Calculated for C₁ <sub>6</sub> H₂ <sub>6</sub> O₄N₃J.H₂O	Found		·10 -
	C%	40.94	40.87		
		5.97	6.02		
15	N%	8.95	8.87		15
	0%	17.06	17.21	•	15
	1%	27.08	27.02	·	

#### THIRD STEP

20 Preparation of 2-hydroxy-3-(2',4'-diaminophenoxy)-propyltrimethylammonium dihydrochloride hemihy-

0.0137 mol (6.2 g) of the quaternary salt obtained in the second step is heated under reflux for 3 hours in 30 ml of ethanol saturated with hydrogen chloride. The expected product precipitates. It is filtered off, washed with absolute alchol and dried in vacuo. It melts with decomposition at between 258 and 260°C.

Elementary analysis gives the following results: 25

25

20

	Analysis	Calculated for C <sub>12</sub> H <sub>22</sub> N <sub>3</sub> O₂CI.2HCI.1l2H <sub>2</sub> O	Found	
30	С%	40.28	40.51	30
	Н%	6.99	6.72	•
•	N%	11.75	1 <b>1.7</b> 7	
	0%	11.19	11.21	
		29.80	29.95	
35				35

#### 35 **EXAMPLE 12**

The following dyeing composition is prepared:

	1-(3'-Nitro-4'-aminophenoxy)-3-aminopropan-2-ol	
40	Hydroxyethylcellulose	
	Ammonium lauryl-sulphate	
	water qs	

The pH of the composition is equal to 8.4. 45 When applied to bleached hair for 20 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a colouration of 7 YR 7/14 (determined on the "Munseil" scale).

45

#### **EXAMPLE 13**

The following dyeing composition is prepared: 50

50

	1-(2'-Amino-4'-nitrophenoxy)-3-aminopropan-2-ol2-Butoxyethanol	0.8 g	
	Acrylic acid polymer having a molecular weight of 2 to 3 million, sold under the name "CARBOPOL 934" "GOODRICH CHEMICAL CO"	" by	55
55	Ammonia solution (220 Bé strength)	2g	JJ
	vages de	ioog	

The pH of the composition is equal t 6.7.

When applied to bleached hair for 35 minut s at 30°C, this mixture imparts to the hair, after rinsing and shamp oing, a colourati n of 3.75 Y 8.5/9.5 (determined nth "Munsell" scale).

	EXAMPLE 14 The foll wing dy ing comp sition is prepar d:	
	1-(3'-Nitro-4'-aminophenoxy)-3-N,N-di thylamino-propan-2-ol hydrochloride	
5	Propylene glycol	5
	Lauric acid	
	Ethylene glycol monoethyl ether	
	Monoethanolamine	
10	Water qs 100 g	10
		10
	The pH of the composition is equal to 7.8.  When applied to bleached hair for 25 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a colouration of 7.5 YR 7/16 (determined on the "Munsell" scale).	
	strain pooring, a colour attorior 7.5 Th 77 to (determined on the Midnsell Scale).	
15	EXAMPLE 15	15
	The following dyeing composition is prepared:	
	1-(2'-Amino-5'-nitrophenoxy)-3-aminopropan-2-ol	
20	Propylene glycol	20
	Lauric acid monoethanolamide 1,5 g	
	Lauric acid '	
	Hydroxyethylcellulose	
2E	Water qs 100 g	
<b>4</b> 5	100 9	25
	The pH of the composition is equal to 10.	
	When applied to bleached hair for 25 minutes at 25°C, this mixture imparts to the hair, after rinsing and	
	shampooing, a colouration of 6.25 Y 8.5/12 (determined on the "Munsell" scale).	
30	PVARADI P 40	30
	EXAMPLE 16 The fellowing of the control of the cont	
	The following dyeing composition is prepared:	
	1-(3'-Nitro-4'-aminophenoxy)-3-N-propylaminopropan-2-ol monohydrochloride 1 g	
35	2 District and hand	35
-	Cetyl/stearyl alcohol sold under the name "ALFOL C16/18" by "CONDEA"	33
	Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL"	
	Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE-POULENC" 1 g	
	Oleic diethanolamide	
40	Ammonia solution (22°C Bé strength)	40
	Water qs 100 g	
	The pH of the composition is equal to 8.7.	
	When applied to bleached hair for 35 minutes at 28°C, this mixture imparts to the hair, after rinsing and	
45	shampooing, a colouration of 7 YR 7/16 (determined on the "Munsell" scale).	45
		43
	EXAMPLE 17	
	The following dyeing composition is prepared:	
	1-{2'-Amino-5'-nitrophenoxy}-3-N-(β-hydroxyethyl)-aminopropan-2-ol	
50	2-Butoxyethanol	50
	Cetyl/stearyl alcohol sold under the name "ALFOL C16/18" by "CONDEA"	
	Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL"	
	Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE-POULENC" 1 g	
55	Oleic diethanolamide	55
	Triethanolamine (containing 10% of active ingredient)	55
	Water qs 100 g	
	The plant the company sister is a much a C.7	
^^	The pH of the comp sition is equal t 8.7.  When appli d to bleach d hair for 30 minut s at 28°C, this mixture imparts t th hair, after rinsing and	
60	shamp oing a colouration of 5 EV9 E/11 Id. to resident to the "Muracilly and shamp oing a colouration of 5 EV9 E/11 Id. to resident to the "Muracilly and the "Muraci	60

# **EXAMPLE 18** The following dyeing comp sition is prepared: Hvdroxyethylcellulose sold under the name "CELLOSIZE WP03" by "UNION CARBIDE" .......2 g Dimethyl-alkyl-hydroxyethyl-ammonium bromide (alkyl = tallow derivative) ...... 2 g Ammonia solution (22° Bé strength) ...... 0.25 g Water qs ...... 100 g 10 The pH of the composition is equal to 8.5. When applied to 90% naturally white hair for 25 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a coppery light chestnut colouration. 15 15 The following dyeing composition is prepared: 3-Nitro-4-N'-(β-aminoethyl)-amino-N,N-di-(β-hydroxyethyl)-aniline dihydrochloride ...... 0.07 g 20 Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "CEMULSOL NP4" by "RHONE-POULENC" ...... 12 g 25 Nonylphenol oxyethyleneated with 9 mols of ethylene oxide, sold under the name "CEMULSOL NP9" by "RHONE-POULENC" ...... 15 g Water qs ...... 100 g 30 The pH of the composition is equal to 8.4. When applied to 90% naturally white hair for 20 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a pinkish beige colouration. 35 35 **EXAMPLE 20** The following dyeing composition is prepared: The pH of the composition is equal to 7. 50 When applied to bleached hair for 20 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a coppery blond colouration. **EXAMPLE 21** The following dyeing composition is prepared: 55

The pH f the composition is equal t 7. When applied to bleached hair for 25 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a g Iden sandy colouration. 5 EXAMPLE 22 The following dyeing composition is prepared: Propylene glycol ....... 10 g Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL" .................... 0.5 g 15 Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE-POULENC" ....... 1 g Triethanolamine (containing 20% of active ingredient) ...... 2 g The pH of the composition is equal to 9. 20 When applied to 90% naturally white hair for 40 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a golden blond colouration. **EXAMPLE 23** The following dyeing composition is prepared: 25 25 Propylene glycol ....... 10 g Hydroxyethylcellulose sold under the name "CELLUSIZE WP03" by "UNION CARBIDE" ......2 g Dimethyl-alkyl-hydroxyethyl-ammonium bromide (alkyl = tallow derivative) ...... 2 g Ammonia solution qs ...... pH 8 Water qs ...... 100 g 35 When applied for 25 minutes at 28°C to hair which has been bleached straw yellow, this mixture imparts to the hair, after rinsing and shampooing, a very coppery chestnut colouration. 40 EXAMPLE 24 40 The following dyeing composition is prepared: 3-Nitro-2-N'-(β-aminoethyl)-amino-N,N-di-(β-hydroxyethyl)-aniline dihydrochloride ....... 0.2 g Hydroxyethylcellulose .......2 g

The pH of the combination is equal to 9.

When applied to bleached hair for 20 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a reddish copper colouration.

Water qs ....... 100 g 50

# **EXAMPLE 25**

The following dyeing comp siti n is prepared:

	The following dyeing composition is prepared:	
	1-{2',4'-Diaminophenoxy}-3-aminopropan-2-ol trihydrochloride	
5	Resorcinol 0.08 g	5
	Para-phenylenediamine	9
	4-Amino-N,N-di-(β-hydroxyethyl)-aniline dihydrochloride	
	3-Nitro-4-amino-N-(β-hydroxypropyl)-aniline	
	3-N-Methylamino-4-nitrophenoxyethanol	
10	Cetyl/stearyl alcohol sold under the name "ALFOL C16/18" by "CONDEA"	10
	Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL"	10
	Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE-POULENC"	
	Oleic diethanolamide 1.5g	
	Pentasodium salt of diethylenetriaminepentraacetic acid, sold under the name "MASQUOL DTPA" 2.5 g	
15	Sodium bisulphite solution (35° Bé strength)	4-
10	Ammonia solution (22° Bé strength)	15
	Water qs 100 g	
	100 g	
	The pH of the composition is equal to 10.1.	
20	100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.	
20	When applied for 30 minutes at 30°C to hair which has been bleached straw yellow, this mixture imparts to	20
	the hair, after rinsing and shampooing, a black-brown colouration.	
	the hair, after thisning and shallipooling, a black-blown colour audit.	
	EXAMPLE 26	
-	The following dyeing composition is prepared:	
25	The following dyeing composition is prepared:	25
	1/2/ A' Diominantoness (2 aminanana 2 alaite da attachaida	
	1-(2'A'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride	
	Resorcinol	
	Meta-aminophenol 0.13 g	
30	Para-phenylenediamine	30
	Para-aminophenol	
	N-Methyl-para-aminophenol sulphate	
	2-Methyl-4-amino-5-nitrophenol	
	Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "REMCOPAL 334"	
35	by "GERLAND"	35
	Nonylphenol oxyethyleneated with 9 mols of ethylene oxide, sold under the name "REMCOPAL 349"	
	by "GERLAND"	
	Oleic acid4g	
	2-Butoxyethanol	
40	Ethanol (96° strength)	40
	Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA" 2.5 g	
	Sodium bisulphite solution (35° Bé strength)	
	Ammonia solution (22° Bé strength)	
	Water qs 100 g	
45		45
	The pH of the composition is equal to 10.5.	
	75 g of hydrogen peroxide of 20 volumes strength are added at the time of use.	
	When applied to 90% naturally white hair for 25 minutes at 30°C, this mixture imparts to the hair, after	
	rinsing and shampooing, an ashen chestnut colouration.	
50		50
	EXAMPLE 27	
	The following dyeing composition is prepared:	
		•
	1-(2',5'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride	
55	2,6-Dimethyl-3-acetylaminophenol	55
	Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "REMCOPAL 334"	
	by "GERLAND"	
	Nonylph nol oxyethyleneat d with 9 mols fethylene oxid, sold under the name "REMCOPAL 349"	
	by "GERLAND"	
60	Ol icacid4g	60
50	2-Butoxyethanol	OU
	Ethanol (96° strength)	
	Pentasodium salt of diethylenetriaminepentraacetic acid, s Id under the nam "MASQUOL DTPA" 3.5 g	
	Ammonia s lution (22° Bé strength) 10 g	
cr	Wat rqs 100 g	~-
03	100 g	65

	The pri of the composition is quartified.  100 g of hydrogen proxide of 20 volumes strength are added at the time of use.  When applied to 90% naturally white hair for 25 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a bluish grey colouration.	
5		5
	EXAMPLE 28 The following dyeing composition is prepared:	
	1-(2',5'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride	
10	2-Methylresorcinol	**
IU	3-Acetylaminophenol	10
	2,4-Diaminophenoxyethanol dihydrochloride	
	3-Nitro-4-amino-6-methyl-N-(β-hydroxyethyl)-aniline	
	1-(3'-Nitro-4'-aminophenoxy)-3-aminopropan-2-ol	
4-	Acrylic acid polymer having a molecular weight of 2 to 3 million, sold under the name "CARBAPOL 934"	
15	by "GOODRICH CHEMICAL CO"	15
	Alcohol (96° strength)	
	2-Butoxyethanol	
	Trimethylcetylammonium bromide	
	Ethylenediaminetetraacetic acid sold under the name "TRILON B"	
20	Ammonia solution (22° Bé strength)	20
	Thioglycolic acid	
	Water qs 100 g	
	100 g	
25	The pH of the composition is equal to 10.  100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.  When applied for 25 minutes at 30°C to hair which has been bleached straw yellow, this mixture imparts to the hair, after rinsing and shampooing, a chestnut colouration.	25
30	EXAMPLE 29	30
	The following dyeing composition is prepared:	
	1-(2',5'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride	
	2,4-Diaminophenyl β-hydroxypropyl ether dihydrochloride	
25	Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "CEMULSOL NP <sub>4</sub> " by	<b></b>
35	"RHONE-POULENC"	35
	Nonylphenyl oxyethyleneated with 9 mols of ethylene oxide, sold under the name "CEMULSOL NP <sub>9</sub> "	
	by "RHONE-POULENC"	
	Oleyl alcohol oxyethyleneated with two mols of ethylene oxide	
40	Oleyl alcohol oxyethyleneated with four mols of ethylene oxide1.5 g	40
40	Propylene glycol	40
	Ethylenediaminetetraacetic acid sold under the name "TRILON B"	
	Ammonia solution (22° Bé strength)	
	Thioglycolic acid	
45	Water qs 100 g	45
. •		
	The pH of the composition is equal to 9.9.	
	100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.	
	When applied to 90% naturally white hair for 30 minutes at 28°C, this mixture imparts to the hair, after	
50	rinsing and shampooing, a pure blue colouration.	50

#### **EXAMPLE 30**

The following dyeing comp sition is prepared:

	The following dyeing comp shorts prepared.	
5	1-(2',4'-Diaminoph noxy)-3-amin propan-2-ol trihydr chl rid	5
10	Oleylamine oxyethyleneated with 12 mols of ethylene oxide, sold under the name "ETHOMEEN TO <sub>12</sub> " by "ARMOUR HESS"	10
15	Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA"	15
20	The pH of the composition is equal to 10.3.  85 g of hydrogen peroxide of 20 volumes strenth are added at the time of use.  When applied to 90% naturally white hair for 25 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a midnight blue colouration.	20
. 25		25
<b>30</b>	1-{2',4'-Diaminophenoxy}-3-aminopropan-2-ol trihydrochloride	30
35	Ammonium lauryl-sulphate containing 30% of active ingredient	35
40	$ \left\{ \begin{array}{cccccccccccccccccccccccccccccccccccc$	40
45	4g   2g   Ammonia solution (22° Bé strength)   11 g   Ethylenediaminetetraacetic acid sold under the name "TRILON B"   1.2 g   Water qs   100 g	45
50	The nH of the composition is equal to 10	50

The pH of the composition is equal to 10.

75 g of hydrogen perioxide of 20 volumes strength are added at the time of use.
When applied to bleached hair for 20 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a pink champagne colouration.

	EXAMPLE 32	
	The following dyeing composition is prepared:	
•	, and the second	
	1-(2',4'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride	
5	Resorcinol 0.15 g	
_	Meta-aminophenol 0.085 g	
	2-Methyl-5-N-(β-hydroxyethyl)-aminophenol	
	Para-phenylenediamine 0.1 g	
	2-Amino-3-nitrophenol	
10	3-Nitro-4-amino-6-methyl-N-(β-aminoethyl)-aniline	10
	Acrylic acid polymer having a molecular weight of 2 to 3 million, sold under the name "CARBOPOL	10
	934" by "GOODRICH CHEMICAL CO" 1.5 g	
	Alcohol (96° strength)	
	2-Butoxyethanol 5g	
15	Trimethylcetylammonium bromide	
10	Ethylenediaminetetraacetic acid sold under the name "TRILON B"	15
	Ammonia solution (22° Bé strength)	
	Thioglycolic acid	
	Water qs 100 g	
20	· · · · · · · · · · · · · · · · · · ·	
20	The pH of the composition is equal to 10.3.	20
	100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.	
	When applied for 30 minutes at 28°C to hair which has been bleached straw yellow, this mixture imparts to	
	the hair, after rinsing and shampooing, a reddish copper medium chestnut colouration.	
25		
29	EXAMPLE 33	25
	The following dyeing composition is prepared:	
	the following dyoling composition to properties.	
	1-(3'-Methylamino-4'-nitrophenoxy)-3-amino-propan-2-ol monohydrochloride	
30	3-Nitro-4-amino-6-methyl-N-(β-hydroxyethyl)-aniline	
50	1,4,5,8-Tetraaminoanthraquinone	30
	2-Butoxyethanol	
	Hydroxyethylcellulose sold under the name "CELLOSIZE WP03" by "UNION CARBIDE"	
	Dimethyl-alkyl-hydroxyethyl-ammonium bromide (alkyl = tallow derivative)	
35	Ammonia solution (5% strength)	05
55	Water qs 100 g	35
	100 Å	
	The pH of the composition is equal to 7.	
	When applied to bleached hair for 20 minutes at 30°C, this mixture imparts to the hair, after rinsing and	
40	shampooing, a light copper colouration.	40
40	siampoong, a ngin copper colouration.	40
	EXAMPLE 34	
	The following dyeing composition is prepared:	
	The lone wing dyonig composition is propared.	
45	1-(3'-Methylamino-4'-nitrophenoxy)-2-aminopropanol monohydrochloride 1 g	45
73	2-Butoxyethanol 10 g	45
	Cetyl/stearyl alcohol sold under the name "ALFOL C16/18" by "CONDEA"	
	Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL"	
	Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE-POULENC"	
E۷	Oleic diethanolamide	~~
50	Triethanolamine (in 20% strength aqueous solution)	50
	Water qs 100 g	
	100 g	
	The pH of the composition is equal to 7.5.	
55		
ວວ	shampooing, a colouration of 4.5 Y 8.5/13 (determined on the "Munsell" scale).	55
	enemptering a established to the following function and the finding of the findin	

# **EXAMPLE 35** The f II wing dy ing composition is prepared: 1-(2',4'-Diamin ph noxy)-3-dimethylaminopr pan-2-ol trihydrochlorid m nohydrate ...... 0.836 g Nonylphenol containing 4 mols of ethylene oxide, sold by "RHONE POULENC" under the name Nonylphenol containing 9 mols of ethylene oxide, sold by "RHONE POULENC" under the name "CEMUSOL NP9" ...... 24 g Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA" ...... 2.5 g Thioglycolic acid ...... 0.6 g Water qs ....... 100 g The pH of the composition is equal to 10.2. 120 g of hydrogen peroxide of 20 volumes strength are added at the time of use. When applied to 90% naturally white hair for 25 minutes at 28°C, this mixture imparts to the hair, after 20 rinsing and shampooing, a midnight blue colouration. The following dyeing composition is prepared: 25 25 2-Hydroxy-3-(2',4'-diaminophenoxy)-propyltrimethylammonium chloride dihydrochloride Para-phenylenediamine ....... 0.108 g Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "REMCOPAL 30 25334" by "GERLAND" ...... 21 g 30 Nonylphenol oxyethyleneated with 9 mols of ethylene oxide, sold under the name "REMCOPAL 2-Butoxyethanol 3g Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA" ..... 2.5 g 40 The pH of the composition is equal to 10. 100 g of hydrogen peroxide of 20 volumes strength are added at the time of use. When applied to 90% naturally white hair for 20 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a bluish grey colouration. 45 The following dyeing composition is prepared: Acrylic acid polymer having a molecular weight of 2 to 3 million, sold under the name "CARBOPOL Ethanol (96° strength) ....... 11 g 2-Butoxyethanol 5g

The pH of the composition is qual to 9.8.

60

100 g of hydrogen peroxide of 20 volumes str ngth are added at th time of use.

When applied f r 25 minutes at 28°C to hair which has been bleach d white, this mixture imparts t th hair, after rinsing and shampooing, a pink shad with a golden sheen.

# **EXAMPLE 38**

The following dyeing comp 'sition is prepared:

	1-(2',4'-Diaminophenoxy)-3-dimethylamino-propan-2-ol trihydr chloride mon hydrate	0.13 g	
5		$0.08\mathrm{g}$	5
_	Para-aminophenol	0.16 a	·
	Resorcinol	0.13 g	
	Meta-aminophenol	0.09 a	
	2-Methyl-5-N-(β-hydroxyethyl)-aminophenol	. 0.1 a	
10	3-N-Methylamino-4-nitrophenoxyethanol	0.03 a	10
10	Oleyl alcohol oxyethyleneated with 2 mols of ethylene oxide	45a	10
	Oleyl alcohol oxyethyleneated with 4 mols of ethylene oxide	450	
	Oleylamine oxyethyleneated with 12 mols of ethylene oxide, sold under the name "ETHOMEEN TO12"	. 4.0 g	
	by "ARMOUR HESS"	450	
15	Diethanolamides of copra fatty acids	. 4.5 y	
15	Propylene glycol	ay	15
	2-Butoxyethanol	4y	
	Ethanol (96° strength)	og	
	Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA"	6g	
	Hydroquinone	2g	
20	Sodium bisulphite solution (35° Bé strength)	U.15 g	20
	Ammonia solution (22° Bé strength)	. 1.3 g	
	Water qs	10 g	
	Marei da	100 g	
	The pH of the composition is equal to 10.		
25	120 g of hydrogen peroxide of 20 volumes strength are added at the time of use.		25
	When applied to 90% naturally white hair for 25 minutes at 28°C, this mixture imparts to the hair, afte		
	rinsing and shampooing, a hazel colouration.	r	
	mising and snampooing, a nazer colouration.		
	EXAMPLE 39		
30	The following dyeing composition is prepared:		30
	The following dyeing composition is prepared.		
	1-(2',A'-Diaminophenoxy)-3-dimethylaminopropan-2-ol trihydrochloride monohydrate	0 2E ~	
	Para-phenylenediamine	0.25 g	
~-	Para-aminophenol	. 0.4 g	
35	2-Methylresorcinol	. U.6 g	35
	2-Methyl-5-N-(β-hydroxyethyl)-aminophenol		
	2-Amino-3-nitrophenol	v.25 g	
	Nonylphenol oxyethyleneated with 4 mols of ethylene oxide, sold under the name "REMCOPAL 334".	. v.z g	
		-	
40	Nonylphenol oxyethyleneated with 9 mols of ethylene oxide, sold under the name "REMCOPAL 349"	21 g	40
	by "GERLAND"		
	Dy GERLAND	24 g	
	Oleic acid	4g	
	2-Butoxyethanol	3 g	
45	Ethanol (96° strength)	10 g	45
	Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA"	. 2.5 g	
	Sodium bisulphite solution (35° Bé strength)	1g	
	Ammonia solution (22° Bé strength)	10 g	
	Water qs	100 g	
50			50
	The pH of the composition is equal to 10.1.		

The pH of the composition is equal to 10.1.

120 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 15 minutes at 30°C to hair which has been bleached straw yellow, this mixture imparts to the hair, after rinsing and shampooing, a coppery chestnut colouration.

# **EXAMPLE 40**

Th following dyeing composition is prepared:

-		
	1-(2',A'-Diaminophenoxy)-3-dimethylamino-propan-2-ol trihydrochloride monohydrate 0.075 g	ı
5	Para-phenylenediamine	5
	N,N-Di-(β-hydroxyethyl)-para-phenylenediamine dihydrochloride	
	N-Methyl-para-aminophenol sulphate	ĺ
	2-Methylresorcinol	1
	Meta-aminophenol	1
10	1-Amino-2-nitro-4-N-(1y-hydroxyethyl)-amino-5-methylbenzene	
	3-Nitro-4-N-(β-aminoethyl)-aminophenoxyethanol	10
	Cetyl/stearyl alcohol sold under the name "ALFOL C16/18E" by "CONDEA"	
-	Sodium cetyl/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL"	
	Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHONE POULENC" 1 g	
15		
	Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA" 2.5 g	15
	Mercaptosuccinic acid	
	Ammonia solution (22° Bé strength)	
	Water qs	
	700 g	
20	The pld of the composition is equal to 0.2	20
	The pH of the composition is equal to 9.3.	
	100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.	
	When applied to 90% naturally white hair for 25 minutes at 25°C, this mixture imparts to the hair, after	
	rinsing and shampooing, a deep chestnut colouration with a coppery sheen.	
25	EVANDE & a	25
	EXAMPLE 41	
	The following dyeing composition is prepared:	
	Otherwood (O) At all all all all all all all all all al	
	2-Hydroxy-3-(2',4'-diaminophenoxy)-propyl-trimethylammonium chloride dihydrochloride	
30	hemihydrate	30
	hemihydrate	
	Nemihydrate	
	hemihydrate	
	hemihydrate	
	hemihydrate	
35	hemihydrate	
35	hemihydrate	
35	hemihydrate	35
35 40	hemihydrate	35
35 40 45	hemihydrate	35 40 45
35 40	hemihydrate	35
35 40 45	hemihydrate	35 40 45
35 40 45	hemihydrate	35 40 45

60

1. A compound represented by the general formula: 55

O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-A

55

or an acid addition salt thereof, in which formula:

10 Z represents NO2 or NH2;

10

5

A denotes NY or

15

40

45

55

15

X<sup>O</sup>, wherein Y represents two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent groups or 20 together with the nitrogen atom of the group

20

25 represents a morpholino or piperidino heterocyclic ring or, when A represents the group NY, Y may also represent two hydrogen atoms or a hydrogen atom and a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent group, Y' represents a C1-C4 alkyl substituent group, and X represents an anion; and

25

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl 30 radical:

30

with the proviso that if A denotes NY (1) if Z is in the 4-position on the benzene nucleus and if NR<sub>1</sub>R<sub>2</sub> is in the 2-position,  $R_1$  and  $R_2$  both representing a hydrogen atom, (a) one of the two substituents of which  $\bar{Y}$  is composed is not an ethyl group if the other substituent is a hydrogen atom and (b) the group NY does not represent a morpholino or piperidino heterocyclic ring, and

(2) If one of the two substituents of which Y is composed denotes a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group 35 and the other denotes a C<sub>1</sub>-C<sub>4</sub> alkyl group and if Z is located in the 3-position, NR<sub>1</sub>R<sub>2</sub> cannot be located in the 2-position when R<sub>1</sub> denotes a hydrogen atom and R<sub>2</sub> denotes a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group.

2. 1-(3'-Nitro-4'-aminophenoxy)-3-N,N-diethylaminopropan-2-ol and its hydrochloride. 1-(3'-Nitro-4'-aminophenoxy)-3-N-propylaminopropan-2-ol monohydrochloride.

1-(3'-Nitro-4'-aminophenoxy)-3-aminopropan-2-ol.

40

1-(2'-Amino-4'-nitrophenoxy)-3-aminopropan-2-ol.

1-(2'-Amino-5'-nitrophenoxy)-3-aminopropan-2-ol.

1-(2'-Amino-5'-nitrophenoxy)-3-N-(β-hydroxyethyl)-aminopropan-2-ol.

8. 1-(2',5'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride. 9. 1-(2',4'-Diaminophenoxy)-3-aminopropan-2-ol trihydrochloride.

45

10. 1-(3'-Methylamino-4'-nitrophenoxy)-3-aminopropan-2-ol hydrochloride.

11. 1-(2',4'-Diaminophenoxy)-3-dimethylaminopropan-2-ol trihydrochloride monohydrate.

2-Hydroxy-3-(2',4',diaminophenoxy)-propyltrimethylammonium chloride dihydrochloride hemihy-12. drate.

13. A process for the preparation of a compound of the formula (I), or salt thereof:

50

55

60 in which:

60

Z repr sents NO2;

Ad notes NY, whir in Y represents two identical ir different C1-C4 alkyl or C1-C4 hydroxyalkyl substituent groups r togeth r with the nitrogen at m of the group NY repr sents a morpholino or piperidino heterocyclic ring, or Y may also represent two hydrogen atoms rahydrogen at mand a C1-C4 alkyl or a

20

30

20

C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent group; and

 $R_1$  and  $R_2$  b th represent hydrog n at ms; with the proviso that if Z is in the 4-position on the benzene nucleus and if  $NR_1R_2$  is in the 2-position,

- (A) one of the two substituents of which Y is comp s d is not an ethyl gr up if the ther substituent is a bydrogen atom and
  - (B) the group NY does not represent a morpholino or piperidino heterocyclic ring, which process comprises:
    - (a) reacting epichlorohydrin with a compound of the formula (II):

to give the compound of the formula (III):

(b) reacting an amine of the formula HNY, in which Y is as defined above, with the compound of the formula (III) to give the compound of the formula (IV):

(c) reacting a strong acid with the compound of the formula (IV) to give the desired compound of the formula (V):

55 Y being as defined above.

14. A process for the preparation of a compound of the formula (I), or salt thereof:

Z represents NH<sub>2</sub>;

A d notes NY, wherein Y r presents two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent groups or t gether with the nitrogen atom f the gr up NY represents a morpholin r pip ridin het r cyclic ring, or Y may also repr sent tw hydrog n at ms or a hydrogen atom and a C<sub>1</sub>-C<sub>4</sub> alkyl or a 5 C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent group, and R<sub>1</sub> and R<sub>2</sub> both represent hydrogen atoms; with the proviso that if Z is in the 4-position on the benzene

5

nucleus and if  $NR_1R_2$  is in the 2-position, (A) one of the two substituents of which Y is composed is not an ethyl group if the other substituent is a hydrogen atom and

(B) the group NY does not represent a morpholino or piperidino heterocyclic ring, which process comprises reducing the nitro group of a compound of formula (V) prepared by a process as claimed in claim 13 to give the desired compound of the formula (VI):

10

15 O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-N-Y
NH<sub>2</sub>
NH<sub>2</sub>

20

15

Y being as defined above.

15. A process for the preparation of a compound of the formula (I), or salt thereof:

25

O-CH<sub>2</sub>-CHOH-CH<sub>2</sub>-A

30

35

in which:

35 Z represents an NO<sub>2</sub> group;

A denotes NY, wherein Y represents two identical or different  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl substituent groups or together with the nitrogen atom of the group NY represents a morpholino or piperidino heterocyclic ring, or Y may also represent two hydrogen atoms or a hydrogen atom and a  $C_1$ - $C_4$  alkyl or a  $C_1$ - $C_4$  hydroxyalkyl substituent group; and

ora yalkyi 40

40 R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or a C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical, except that both R<sub>1</sub> and R<sub>2</sub> do not simultaneously represent a hydrogen atom; which process comprises

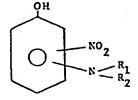
reacting epichlorohydrin with a compound of the formula (VII):

45

50

25

30

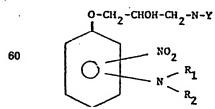


45

and reacting an amine of the formula HNY, in which Y is as defined above, with the compound thus obtained to give the desired compound of the formula (VIII):

55

50



### 16. A process for the preparation of a compound of the formula (I), r salt thereof:

O-CH\_-CHOH-CH\_-A 5 10

10

5

in which:

Z represents an NH<sub>2</sub> group;

A denotes NY, wherein Y represents two identical or different C1-C4 alkyl or C1-C4 hydroxyalkyl substituent 15 groups or together with the nitrogen atom of the group NY represents a morpholino or piperidino heterocyclic ring, or Y may also represent two hydrogen atoms or a hydrogen atom and a C1-C4 alkyl or a C1-C4 hydroxyalkyl substituent group; and

15

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical except that both R<sub>1</sub> and R<sub>2</sub> do not simultaneously represent a hydrogen atom; which process reducing the nitro group of a compound of formula (VIII) prepared by a process as claimed in claim 15 to give

20

the desired compound. 17. A process according to claims 14 or 16 wherein reduction of the nitro group is carried out either by means of zinc powder in an alcoholic medium in the presence of ammonium chloride or by means of

25

25 catalytic hydrogenation. 18. A process for the preparation of a compound of the formula (I), or salt thereof:

30

35

35

30

in which:

Z represents an NH<sub>2</sub> group;

A denotes NY, Y represents two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent groups 40 or the group NY represents a morpholino or piperidino heterocyclic ring; and

40

 $R_1$  and  $R_2$  are identical or different and represent a hydrogen atom or a  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl radical except that both R<sub>1</sub> and R<sub>2</sub> do not simultaneously represents a hydrogen atom; which process comprises introducing one or two C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituents onto one of the nuclear amine groups of a compound of the formula (VI) prepared by a process as claimed in claim 14.

19. A process according to claim 18, wherein the or both substituents are introduced into the corresponding arylsulphonamide and the thus-substituted arylsulphonamide is hydrolysed.

45

20. A process for the preparation of a quaternary compound of the formula (I):

50

55

65

55

50

in which:

Zis NO2 or NH2;

A den tes

60

 $X^{\Theta}$  wherein Y represents two identical or different  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl substituent groups or together with the nitregen atom of the group

5 N⊕ Y

5

10

15

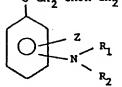
represents a morpholino or piperidino heterocyclic ring, Y' represents a C<sub>1</sub>-C<sub>4</sub> alkyl substituent group and X represents an anion; and

R<sub>1</sub> and R<sub>2</sub> are identical or different and represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical;
which process comprises protecting the or each nuclear amine group of a corresponding compound of the formula (I) wherein Δ represents NY by acceptation, reacting the protected compound with a question of the question of the protected compound with a question of the question of the question of the question of the question of t

which process comprises protecting the or each nuclear amine group of a corresponding compound of the formula (I) wherein A represents NY by acetylation, reacting the protected compound with a quaternising agent and deacetylating with an acid the quaternised compound.

- 15 21. A process according to claim 20, wherein methyl iodide is used as the quaternising agent.
  22. A process for the preparation of a compound of formula (I), or salt thereof.
  - said process being substantially as hereinbefore described in any one of Examples 1 to 11.
  - 23. A dyeing composition suitable for keratin fibres and in particular for hair, which composition comprises at least one compound, or salt thereof, of the formula (I)

9-сн<sub>2</sub>-снон-сн<sub>2</sub>-а



25

20

in which formula:

25

Z represents a nitro group; A represents a group NY or

30

35 <sup>®</sup> N

35

 $X^{\Theta}$  wherein Y represents two identical or different  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl substituent groups or together with the nitrogen atom of the group NY or

40

45

$$N \oplus <_{Y}^{Y}$$

represents a morpholino or piperidino heterocyclic ring or, when A represents the group NY, may also represent two hydrogen atoms or a hydrogen atom and a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl substituent group, Y' represents a C<sub>1</sub>-C<sub>4</sub> alkyl substituent group and X represents an anion; and

 $R_1$  and  $R_2$  are identical or different and each represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  hydroxyalkyl radical;

together with an appropriate carrier.

50

55

60

- 24. A dyeing composition suitable for keratin fibers and in particular for hair, which composition comprises at least one compound of the formula (I), or salt thereof, as defined in claim 23 except that Z represents an NH<sub>2</sub> group in the ortho- or para-position relative to NR<sub>1</sub>R<sub>2</sub>, together with an appropriate carrier.
  - 25. A composition according to claim 24 which contains an oxidising agent at the time of use.
  - 26. A composition according to any one of claims 23 to 25 wherein the compound of the formula (I) is present in the composition in an amount of from 0.001 to 4% by weight, relative to the to tall weight of the composition.

	together with an appropriate carrier and at least one oxidation base.	
	28. A composition according to claim 27 which contains an oxidising agent at the time of use.	
	29. A compositi in according to claim 27 or 28 wherein the compound of the formula (I) is present in the	
	composition in an amount ffr m 0.001 to 2.5% by weight, relativ to th total weight of the composition.	
5	30. A composition according to any one of claims 23 to 29 which contains at least one exidation base	5
	selected from para-phenylenediamines, para-aminophenols or heterocyclic bases.	•
	31. A composition according to any one of claims 23 to 30 which contains at least one coupler selected	
	from resorcinol, pyrocatechol, 2-methylresorcinol, 2-ethylresorcinol, meta-aminophenol, 2-methyl-5-	
	aminophenol, 2-methyl-5-N-(β-hydroxyethyl)-aminophenol, 6-hydoxybenzomorpholine, 2,6-dimethyl-3-	
10	acetylaminophenol, 2-methyl-5-carbethoxyaminophenol, 2-methoxy-5-carbethoxyaminophenol, 2-methyl-	10
	5-ureidophenol, 2,4-diaminophenoxyethanol, 2,4-diaminoanisole, 2,6-dimethylmeta-phenylenediamine, 2-	
	amino-4-N-methylaminophenoxyethanol, 2,4-diaminophenyl β-methoxyethyl ether, 2,4-diaminophenyl β-	
	mesylaminoethyl ether, 2-N-carbamylmethylamino-4-amino-anisole, 3-amino-4-methoxyphenol, α-	
	naphthol, 2,6, diaminopyridine, 3,5-diamino-2,6-dimethoxypyridine, 1-phenyl-3-methylpyrazol-5-one and	
15	2-amino-4-N-(β-hydroxyethyl)-aminophenyl β-hydroxypropyl ether.	15
	32. A composition according to any one of claims 23 to 31, which contains a compound selected from	
	ortho-diphenol, ortho-phenylenediamines and orthoaminophenols, the ortho-phenylenediamines and	
	orthoaminophenols being unsubstituted or substituted on the nucleus or on the amino group(s).	
	33. A composition according to any one of claims 23 to 32 which contains a dyestuff precursor of the	
20	bezene series, containing, on the nucleus, at least three substituents selected from hydroxyl, methoxy and amino.	20
	34. A composition according to any one of claims 23 to 33 which contains a quinone dyestuff.	
	35. A composition according to any one of claims 23 to 34, which contains an indoaniline, indophenol,	
	indamine or a leuco derivative thereof.	
25	36. A composition according to any one of claims 23 to 35, which contains a dyestuff selected from azo	
25	dyestuffs, anthraquinone dyestuffs and nitro dyestuffs of the benzene series.	25
	37. A composition according to any one of claims 23 to 36, which has a pH of from 5 to 11.5.	
	38. A composition according to any one of claims 23 to 37, which contains at least one adjuvant selected	-
	from penetrating agents, surface-active agents, thickeners, antioxidants, alkalising or acidifying agents,	
30	perfumes, sequestering agents, film-forming products, treating agents and solvents.	30
	39. A composition according to any one of claims 23 to 38, which is in the form of a liquid, a cream, a gel	
	or an aerosol.	
	40. A dyeing composition substantially as hereinbefore described in any one of Examples 12 to 41.	
	41. A hair-dyeing process comprising leaving a composition as claimed in claim 23 to act on the hair for	
35	an application time of from 10 to 45 minutes, rinsing the hair, optionally washing and rinsing the hair again,	35
	and drying the hair.	
	42. A process according to claim 41, in which the dyeing composition used contains at least one	
	oxidation base and at the time of use, a sufficient amount of oxidising agent is added to the dyeing	
	composition used.	
40	43. A hair-dyeing process substantially as hereinbefore described in any one of Examples 12 to 41.	40